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(54) Title: NON TOXIC, BIODEGRADABLE WELL FLUIDS

(57) Abstract

Well fluids such as drilling muds, especially useful in offshore drilling, are formulated with a hydrocarbon oil blend of a low viscosity poly alpha-olefin (PAO) such as a low molecular weight oligomer of decene together with a C_{12} to C_{18} paraffinic hydrocarbon of petroleum origin and a C_{10} to C_{18} olefin such as dodecene-1 or tetradecene-1. The fluids exhibit good biodegradability and are non-toxic to marine organisms; they also meet viscosity and pour points specifications for formulation into oil based muds.

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NON TOXIC, BIODEGRADABLE WELL FLUIDS

The present invention relates to well fluids, especially to drilling fluids or muds which are useful in the rotary drilling process used for making wells into subterranean formations containing oil, gas or other minerals. In particular, the invention relates to a drilling mud which contains a hydrocarbon oil of reduced marine toxicity and improved biodegradability.

The rotary drilling process is used for making wells for the production of oil, gas and other subterranean minerals such as sulfur. In rotary drilling operations, a drill bit at the end of a drill string is used to penetrate the subterranean formations. This drill bit may be driven by a rotating drill string or a drill motor powered, for example, by hydraulic power. During the rotary drilling operation, a fluid, conventionally referred to as drilling mud, is circulated from the drilling equipment of the surface down to the drill bit where it escapes around the drill bit and returns to the surface along the annular space between the drill bit and the surrounding subsurface formations. The drilling mud lubricates the downhole equipment and brings the formation cuttings to the surface where they can be separated from the mud before it is recirculated. In addition, the drilling mud serves to counterbalance formation pressures and may also form a cake around the walls of the borehole to seal the formations. The lubricating action of the drilling mud is particularly important with the conventional rotating drill string since it provides a lubricant or cushion between the rotating drill pipe and the walls of the borehole, helping to prevent sticking of the drill string in the hole. The characteristics and performance of drilling muds are described, for example, in Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition, John Wiley and Sons, 1982, under Petroleum (Drilling Muds), to which reference is made for a description of drilling muds and the materials used in formulating them.

Drilling muds are usually classified as either water-based muds or oil-based muds, depending upon the character of the continuous phase of the mud, although water-based muds may

contain oil and oil-based muds may contain water. Water-based muds conventionally comprise a hydratable clay, usually of the montmorillonite family, suspended in water with the aid of suitable surfactants, emulsifiers and other additives including salts, pH control agents and weighting agents such as barite. The water makes up the continuous phase of the mud and is usually present in an amount of at least 50 percent of the entire composition; oil may be present in minor amounts but will typically not exceed the amount of the water so that the mud will retain its character as a water-continuous phase material. Oil-based muds on the other hand, generally use a hydrocarbon oil as the main liquid component with other materials such as clays or colloidal asphalts added to provide the desired viscosity together with emulsifiers, gellants and other additives including weighting agents. Water may be present in greater or lesser amounts but will usually not be greater than 50 percent of the entire composition; if more than about 10 percent water is present, the mud is often referred to as an invert emulsion, i.e a water-in-oil emulsion. In invert emulsion fluids, the amount of water is typically up to about 40 weight percent with the oil and the additives making up the remainder of the fluid.

Oil-based muds are conventionally formulated with diesel oil or kerosene as the main oil component as these hydrocarbon fractions generally posses the requisite viscosity characteristics. They do, however, posses the disadvantage of being relatively toxic to marine life and the discharge of drilling muds containing these oils into marine waters is usually strictly controlled because of the serious effects which the oil components may have on marine organisms, particularly those which are commercially important for food. For this reason, offshore drilling rigs must return oil-based muds to shore after they have been used whereas water-based muds may generally be discharged into the ocean without any deleterious effects.

Oil-based muds may be made environmentally acceptable by the use of oils which posses low inherent toxicity to marine

organisms and good biodegradability. These properties are associated in hydrocarbons with low aromaticity. For these reasons, drilling fluids based on linear paraffins might be considered desirable. On the other hand, however, the linear paraffins tend to have high pour points and the higher molecular weight fractions tend to be waxy so that in the low temperature environments frequently encountered in offshore drilling, there is a significant risk that waxy paraffin deposits will be formed in the downhole equipment or in the riser connecting the sea bed to the drilling equipment. In either event, this is unacceptable so that highly paraffinic oils have not achieved any significant utility as the base fluids in oil based muds.

We have now found that drilling muds and other well treatment fluids may be formulated to have improved levels of biodegradability and low marine toxicity together with other advantageous properties by using a mixed mineral oil olefinic-paraffinic hydrocarbon component containing from 10 to 18 carbon atoms in addition to a PAO. This paraffinic-olefinic mixture is made up of C_{10}-C_{18} paraffins in combination with C_{10}-C_{18} olefins to give a blend of the correct viscometrics. With the PAO component present, the hydrocarbon oil has a viscosity of 1 to 4 cS at 100C (ASTM D-445), a flash point of at least 70C, and a pour point no higher than +5C.

According to the present invention, well fluids such as drilling fluids used in the rotary drilling of wells into subterranean formations for the production of oil, gas and other minerals, are formulated with an oil component which is a hydrocarbon blend of a mixed petroleum-based (mineral oil origin) paraffinic-olefinic component and a synthetic PAO component of low viscosity. The blended oil component has a viscosity of 0.5, for example 1, to 4 cS, preferably 0.7 to 2 cS at 100C (ASTM D-445) and a viscosity of 1.0 to 30 cS, preferably 2.0 to 20 cS, at 40°C and a flash point (ASTM D-93) of at least 70C, preferably at least 100C or higher, for example, at least 120C. Pour point (ASTM D-97) should be no higher than +5C, for example from -60 to +5°C, preferably no higher than 0 or even -5C. The specific gravity of the oil is

in the range 0.75 to 0.82. at 60F (15.6C)(ASTM D-1298)

The mineral oil component of the hydrocarbon blends which are used in the present non-toxic well fluids is produced from conventional mineral oil sources and is essentially a mixture of C_{10}-C_{18} n-paraffins and C_{10}-C_{18} olefins of low viscosity suitable for formulation into the well fluids after the addition of the PAO component.

The olefinic component of the blend is normally a C_{12}-C_{16} olefin, usually an alpha-olefin such as 1-dodecene or 1-tetradecene, for a suitable balance of pour point, flash point and viscosity in the final oil component. The amount of the olefin in the hydrocarbon blend is usually in the range of 5 to 75 weight percent and in most cases, from 10 to 60 weight percent of the blend. Normally, from 15 to 30 weight percent of the olefin component will be preferred.

The C_{10}-C_{18} paraffins make up the bulk of the hydrocarbon blend and are usually n-paraffins although minor amounts of iso-paraffins and cycloparaffins may be present as impurities. The paraffinic mixtures typically contain at least 98 weight percent n-paraffins and are essentially free of aromatics (less than 1 and preferably less than 0.5, weight percent monocyclic aromatics). The paraffinic component need not include paraffins across the entire C_{10}-C_{18} range but may be more limited in terms of carbon number in order to provide the desired viscometrics. Typical paraffinic mixtures for blending with the olefinic component and the PAO component are shown below. One is a C_{10}-C_{13} mixture with a low viscosity, pour point and flash point while the other two are higher carbon number (C_{12}-C_{14}, C_{14}-C_{18}) mixtures with correspondingly higher pour points, flash points and viscosities. Paraffinic mixtures such as these may be used either as such or as blends with each other to achieve the desired properties in the final hydrocarbon blend. The amount of the paraffin component will normally be in the range of 20 to 90 weight percent of the blend, and in most cases in the range of 30 to 75 weight percent.

Paraffin Hydrocarbons

Physical Properties	ASTM	Paraffin-A	Paraffin-B	Paraffin-C
Viscosity @ 38°C	D-445	1.37	1.93	2.42
25°C	D-445	1.68	2.41	3.27
Pour Point °C	D-97	-21	-4	7
Spec. Gravity @ 15.6°C	D-1298	0.751	0.764	0.771
Flash Point °C	D-93	69	93	118
Composition, mass %	Mass spec			
Normal Alkanes		98.1	98.7	99.4
C10		13	-	-
C11		36	-	-
C12		44	12	-
C13		7	60	
C14		-	28	32-34
C15		-	-	42-45
C16		-	-	16-18
C17		-	-	4-6
C18		-	-	1-3
Isoparaffins		0.2	0.6	0.6
Cycloparaffins		1.1	0.6	0.6
Mono-Aromatics	U.V.	0.6	0.2	0.01

In addition to the petroleum-based paraffin and olefin components, the well fluids also contain a poly alpha-olefin oligomer (PAO). This component is produced by the oligomerization of a 1-olefin, typically with the use of a cationic catalyst such as a Lewis acid catlyst, for example, born trifluoride or aluminum chloride. Boron trifluoride is preferred as the catalyst since it is a liquid phase, homogeneous catalyst which readily produces the low molecular weight, low viscosity oligomers which are used in the present well fluids. PAOs are well-known materials and are commercially available from a number of sources. Processes for making them are described, for example, in U.S. Patents Nos. 3,780,128 (Shubkin), 4,405,507 (Cupples) and 4,405,508 (Cupples). PAOs of low viscosity are also described in U.S. 4,956,122 (Watts). The olefin monomers which are conventionally used in the production of PAOs are the 1-olefins containing from 6 to 20 carbon atoms, preferably from 8 to 18 carbon atoms, especially from 8 to 12 carbon atoms, with particular preference given to 1-decene since the oligomer products have a particularly favorable balance of properties. The olefin oligomers typically possess some residual unsaturation after the oligomerization has taken place and if desired, the oligomers may be hydrogenated prior to use in the present fluids but it is not essential to do so. Bromine numbers on the as-synthesized oligomers are typically in the range of 30 to 50 and less than 5, usually less than 2 for the hydrogenated materials. Both the hydrogenated and unhydrogenated oligomers of this type possess good biodegradability.

The PAO components used in the present fluids are the low molecular weight oligomers, preferably dimers or mixed dimer/trimer, of the olefins described above. Normally, these PAOs are predominantly C_{20} to C_{50} polyolefins. The molecular weight of the selected PAO will depend on the desired viscometrics for the drilling fluid; the lower molecular weight oligomers have lower viscosities. The PAO oligomers typically have a viscosity in the range of 1 to 6 cS (100C), more typically in the range of 1 to 4 cS (100C). Flash points are

usually above 150C for this component. The structure of these oligomers confers good low temeperature properties, as indicated by pour points (D-97) below -40C and in most cases below -50 or -60C. Typical PAOs which may be used in the present fluids are polydecenes having approximately the following properties:

			PAO-A	PAO-B
Viscosity:	D-445	100°C	1.7	2.4
	D-445	40°C	5	8
	D-445	-40°C	260	625
Pour Point,	D-97	°C	-65	-62
Flash Point,	D-93	°C	160	170

PAO-A is essentially a decene-1 dimer (over 98% C_{20}) while PAO-B is a decene-1 mixed dimer-trimer (over 97.5% C_{20}-C_{30}), with a dimer-tetramer ratio of about 1.35:1. Other similar PAO materials may be used in the present fluids provided that the desired properties are achieved in the final composition.

The PAO component is used in an amount from 3 to 80 weight percent, typically from 15, for example 7, to 25, preferably from 10 to 20, weight percent of the total hydrocarbons in the oil component of the mud.

The paraffinic hydrocarbon component comprises a fraction in the C_{10}-C_{18} range; for example, the C_{14}-C_{18} range, the C_{12}-C_{16} range, the C_{12}-C_{14} range or the C_{10}-C_{14} range.

The olefinic hydrocarbon component comprises a fraction in the C_{10}-C_{18} range; for example, the C_{12} to C_{18} range or the C_{12}-C_{16} range; preferably it comprises 1-dodecene or 1-tetradecane.

The composition of the hydrocarbon blend including both the C_{12}-C_{18} component as well as the C_{20} and higher components from the PAO, is given below.

Well Fluid Hydrocarbons

Hydrocarbon	Min.	Max.	Pref. Min.	Pref. Max.	Typical
Paraffinic/Olefinic Components					
Dodecene	0	3	0.5	2	1
Tetradecane	5	20	10	20	18
Tetradecene	10	60	10	30	19
Pentadecane	5	30	15	30	26
Hexadecane	3	15	3	15	10
Hexadecene	0	0.5	0.5	2	1
Heptadecane	0	5	1	5	3
Octadecene	0	0.5	0.5	2	1
PAO Components					
Eicosane	5	50	5	15	12
Triacontane	2	40	5	10	8
Tetracontane	0	5	0.5	2	1

The oil component is formulated into drilling muds or other well treatment fluids such as completion fluids. Formulation will, with the exception of the choice of the specific oil component as the hydrocarbon base fluid, be conventional in type and normal types of additives including emulsifiers, surfactants, viscosity-modifying agents, weighting agents and other components will be suitable. The density of the muds will typically be in the normal range of 6 to 28 pounds per gallon.

The preferred type of muds using the present oils are oil-based muds, especially the invert-emulsion type muds which contain water disperesed in the oil component which makes up the contiuous phase of the final emulsion-type mud. In muds of the invert emulsion type, the amount of oil in the final mud will typically be from 25 to 75% by weight, and is typically in the range of 40 to 60% by weight of the final mud. The balance of the mud typically comprises water and the normal additives such as clays, salts such as sodium chloride, calcium chloride or calcium bromide, weighting agents such as barite or hematite (high density fluids) or dolomite or calcite (low density fluids such as completion and work-over fluids), viscosity modifiers, pH control agents, circulation control agents such as ground seed hulls or shredded cellulosic materials and other additives

wehich may be conventional in type. When the oil component is formulated into the mud, conventional blending procedures are used, for example, blending the oil with the emulsifiers and surfactants, followed by mixing with water in the requisite amounts to form the final invert (water-in-oil) emulsion which may then be blended with other additives, as necessary.

If the oil component is used in water-based muds, it would appropriately be used in an amount of up to 50 weight percent of the mud with the other components being water and conventional type additives, as described above.

The well fluids based on these paraffin/olefin/PAO blends may be used as drilling muds in rotary drilling as well as in other well operations, for example, for filling the well during testing, completion work-over, in the same way as other muds and well treatment fluids. the fluids based on the present oils have, however, the particular advantage that in offshore drilling operations, cuttings contaminated with the fluids may be disposed of by discharge into the sea. The good biodegradability and non-toxicity of the present muds permits this type of cuttings disposal in the ocean environment without any significant risk of persistent pollution.

The folowing Examples illustrate the preparation and testing of well fluids according to the present invention. In all the Examples, the oil component, identified as Oil-C was a blend of 60 weight percent of a C_{14}-C_{18} paraffinic hydrocarbon oil (Paraffin-C above) and 20 weight percent of tetradecene (99.6 percent 1-olefins, 95.5 percent C_{14}, 2.5 percent C_{16}) together with 20 weight percent of a 2-4 cS PAO prepared by the oligomerization of 1-decene using a boron trifluoride catalyst (PAO-B above). The final oil blend had the composition set out in the table below, where the C_{12}-C_{18} components are derived from the paraffinic oil and the olefin and the C_{20} and higher components come from the PAO.

Hydrocarbon Blend, wt. pct.

Dodecene	1
Tetradecene	20
Tetradecane	20
Pentadecane	25
Hexadecane	10
Heptadecane	3
Octadecane	1
Eicosane	11
Triacontane	8
Tetracosane	1
	100

Example 1

A series of differently weighted 40/60 oil/water muds (10, 12, 14 pounds per gallon - ppg) were made with the oil blend and the following components:

Emulsifier	Ezmul NT (Baroid)
Rheology Modifier	RM 63 (Baroid)
Fluid Loss Additive	Duratone HT (Baroid)
Organoclay	Geltone II (Baroid)

The formulations are set out in the table below.

40/60 Oil/Water Mud

		10 ppg	12 ppg	14 ppg
Oil C	(bbl)	0.325	0.303	0.275
Ezmul NT	(ppb)	8.0	8.0	8.0
Duratone HT	(ppb)	2.0	2.0	2.0
Lime	(ppb)	4.0	4.0	4.0
Geltone II	(ppb)	1.0	1.0	0.5
Water	(bbl)	0.504	0.464	0.425
$CaCl_2$ (82%)	(ppb)	77.0	71.4	65.3
RM63	(ppb)	2.0	-	-
Barite	(ppb)	61.5	173.4	285.5

These muds were tested for the following properties, using the test conditions specified:

Property		Test Conditions
Apparent Viscosity	(AV)	cps, 600 rpm reading/2 120F
Plastic Viscosity	(PV)	cps, 120F
Yield Point	(YP)	lb/100 sq. ft., 120F
Gel Strength	(Gel)	10sec./10min., 120F
Electric Strength	(ES)	volts, 120F

These properties were determined both before (BHR) and after (AHR) hot rolling at250F for 16 hours. All rheologies and ES were measured at 120°F.

The properties of the muds are shown below.

Mud Properties

	10 ppg		12 ppg		14 ppg	
	BHR	AHR	BHR	AHR	BHR	AHR
AV	108.5	83.5	116	116	127	123
PV	64	64	86	84	98	95
YP	89	39	60	64	58	56
Gel	40/55	14/18	21/22	19/20	18/21	17/18
6 rpm	45	17	25	24	24	21
ES	305 V	414 V	414 V	360 V	360 V	387 V
HTHP @ 250°F	-	2.4 mls	-	12.8 mls inc 6 mls H_2O	-	13.6 mls inc 6.4 mls H_2O

Note
The high HTHPs may be due to the RM 63 being removed from the formulation for the 12 and 14 ppg muds.

Example 2

A series of 55/45 oil/water muds were formulated and tested as in Example 1. The formulations and test results are given below.

55/45 Muds

		10 ppg	12 ppg	14 ppg
Oil C	(bbl)	0.42	0.415	0.379
Ezmul NT	(ppb)	8.0	8.0	8.0
Duratone HT	(ppb)	2.0	2.0	2.0
Lime	(ppb)	4.0	4.0	4.0
Geltone II	(ppb)	4.0	2.5	1.0
Water	(bbl)	0.375	0.345	0.316
$CaCl_2$ (82%)	(ppb)	57.7	53.1	48.5
RM63[2]	(ppb)	2.0	2.0	2.0
Barite	(ppb)	89.5	199.7	310.0

Mud Properties

	10 ppg		12 ppg		14 ppg	
	BHR	AHR	BHR	AHR	BHR	AHR
AV	51	43	60.5	44	68	54.5
PV	33	38	37	39	40	45
YP	36	10	47	10	56	19
Gel	19/30	12/22	25/53	10/21	20/30	14/22
6 rpm	21	10	25	10	23	15
ES	331 V	291 V	467 V	417 V	448 V	456 V
HTHP @ 250°F	-	3.6 mls	-	3.8 mls	-	1.0 mls

Example 3

A series of differently weighted 75/25 oil/water muds (12, 14, 16 ppg) were made and tested as in Example 1. The results are given below.

75/25 Muds

		12 ppg	14 ppg	16 ppg
Oil C	(bbl)	0.550	0.497	0.445
Ezmul NT	(ppb)	10.0	10.0	10.0
Duratone HT	(ppb)	6.0	6.0	6.0
Lime	(ppb)	4.0	4.0	4.0
Geltone II	(ppb)	8.0	6.0	4.0
Water	(bbl)	0.191	0.175	0.158
$CaCl_2$ (82%)	(ppb)	29.4	26.9	24.4
RM63	(ppb)	2.0	2.0	2.0
Barite	(ppb)	227.3	333.8	440.3

Mud Properties

	12 ppg		14 ppg		16 ppg	
	BHR	AHR	BHR	AHR	BHR	AHR
AV	48	29	59	37	72	45.5
PV	31	24	38	32	49	38
YP	34	10	42	10	46	15
Gel	24/35	6/15	27/36	7/15	25/37	9/17
6 rpm	22	6	28	7	26	8
ES	1101 V	458 V	1225 V	513 V	1344V	723 V
HTHP @ 250°F	-	54 mls inc 13.4 mls H_2O /Emulsion	-	47.4 mls inc 10 mls H_2O /Emulsion	-	23.8 mls Trace H_2O

Example 4

A series of differently weighted (14, 16, 18 ppg) 80/20 oil/water muds were made and tested as in Example 1. The results are given below.

80/20 Muds

		14 ppg	16 ppg	18 ppg
Oil C	(bbl)	0.524	0.469	0.416
Ezmul NT	(ppb)	12.0	12.0	12.0
Duratone HT	(ppb)	7.0	7.0	7.0
Lime	(ppb)	4.0	4.0	4.0
Geltone II	(ppb)	7.0	5.0	3.0
Water	(bbl)	0.138	0.126	0.113
$CaCl_2$ (82%)	(ppb)	21.3	19.4	17.4
	(ppb)	2.0	2.0	2.0
Barite	(ppb)	344.5	451.4	558.2

Mud Properties

	14 ppg		16 ppg		18 ppg	
	BHR	AHR	BHR	AHR	BHR	AHR
AV	50	30	68	53.5	95	68.5
PV	34	25	50	38	72	60
YP	32	10	36	11	46	17
Gel	18/32	8/14	21/35	8/16	25/35	10/23
6 rpm	18	6	22	7	25	9
ES	1575 V	736 V	1526 V	976 V	1425 V	959 V
HTHP @ 250°F	-	26.2 mls Trace H_2O	-	37.6 mls	-	32.2 mls

Example 5

The toxicity of the base oil (Oil C) and two formulated drilling muds was evaluated using organisms representing two trophic levels (Skeletonema costatum, algae and Acartia tonsa, herbivorous crustacean). Tests were conducted on the dissolved phase of seawater extracts of the three materials, in accordance with ISO/PARCOM protocols (Toxicity Test with Marine Unicellular Algae:Technical Support Document for the ISO DP 10253 Standard Method; Proposal to TC147/SC5/WG2: Determination of Acute Lethal Toxicity to Marine Copepods (Copepoda; Crustacea)).

Skeletonema

The effect of the test material was assessed by measuring the degree to which the cell culture growth rate was inhibited. This is expressed as the EC_{50} value; the concentration which reduces growth rate to 50% with respect to the growth rate of control cultures. The test is of 72 h duration, and the intrinsic daily growth rates of cultures are calculated over 24, 48 and 72 h. Duplicate cultures were tested in media prepared from nutrient-enriched seawater to which a range of quantities of the test material had been added.

Rangefinding tests were conducted at 20°C over 24 h in media prepared from additions of 10, 100, 100 and 10000 mg/l (base oil) or 10, 32, 100 and 320 mg/l (formulated muds). These tests indicated that the base oil was non-toxic at 10000 mg/l added substance, and that the formulated muds were not toxic at 320 mg/l added test substance.

Definitive tests were conducted on the formulated muds at addition rates of 1000, 1800, 3200 and 5600 mg/l. The 48 h and 72 h LC_{50s} for an oil mud formulated using additives from MI GB Ltd (referred to below as "MI mud") were estimated to be 4095 and 4983 mg/l respectively, while the 48 h and 72 h LC_{50s} for an oil mud formulated using additives from BW Mud Ltd. (referred to below as "BW mud") was estimated to be 4820 and 5971 mg/l respectively.

Acartia

Effects on Acartia were assessed in terms of the proportion of individuals dead or immobile after 24 h and 48 h exposure to the test medium, and are expressed as an LC_{50} value; the concentration at which 50 % of a test population is killed or immobilized. Adult Acartia (27 days old) were exposed in groups of five in 100 ml crystallizing dishes containing 50 ml of test medium. In rangefinding tests, five animals per concentration were exposed for 24 h at 20°C. In definitive tests, twenty animals were exposed (in four replicates of five) for 48 h under the same conditions.

Test media were prepared by direct addition of the test substance to 0.45 μm-filtered seawater. In the rangefinding tests, additions of 1, 10, 100, and 1000 mg/l were prepared. In definitive tests, additions of 100, 1800, 3200 and 5600 mg/l were prepared.

The base oil and MI mud were not toxic at the highest concentrations tested (5600 mg/l). Mortality was observed at the 5600 mg/l with BW mud, and an approximate LC_{50} of 5400 mg/l was estimated graphically using a log-probability plot.

From these observations it was concluded that the three materials tested (base oil, two muds) were of low toxicity to both test organisms. There was some evidence that the formulated muds were more toxic than the base oil. Both muds were of similar toxicity, although the small degree of response did not permit precise calculation or comparison of effects concentrations.

Toxicity Test Results

Skeletonema

The starter culture characteristics and the initial inoculum data for the rangefinding tests were as follows:

Starter culture inoculation: 10^3 cells/ml
Starter culture cell count at 96h: $9.6*10^5$ cells/ml
Initial test inoculum: $0.29\ \mu m^3.10^6$

The average control growth rate in the rangefinding tests was $1.11\ d^{-1}$. The rangefinding tests indicated that the test material preparations were not toxic (growth was not reduced with respect to the controls) over 24 h at the highest concentrations tested - 10000 ppm in the case of the base oil and 320 ppm in the case of the formulated muds (Table 3). Accordingly, definitive tests were conducted on the muds at addition rates between 1000 and 5600 mg/l.

The starter culture characteristics and the initial inoculum data for the definitive tests were:

Starter culture inoculation: 10^3 cells/ml
Starter culture cell count at 96h: $5.1*10^5$ cells/ml
Initial test inoculum: 103 cells/ml, $0.12\ \mu m^3.10^6$

Raw observations of algal cell volume were made at 24, 48 and 72 h in the definitive tests. Contol growth rate was maintained above the guideline value of 0.9 d^{-1} throughout the tests. Measurements of pH made in all vessels at the start and end of the test, and in controls at 24 h intervals, indicated that values lay between 8.09 and 8.21, and did not vary systematically between test substances or between concentrations.

Both muds were of similar, low toxicity. EC_{50} values were estimated using the moving average-angle method and are shown below.

EC_{50} Values for Muds

Test Substance	EC_{50} (mg/l added test subst.) 48 h.	72h.
MI Mud	4090	4980
BW Mud	4820	5970

Acartia

No mortality was observed in rangefinding tests at any addition rate of any test mud between 1 and 1000 mg/l.

The results of the definitive tests are presented in Table 8. After 24 h, mortality did not exceed 10 % in any treatment, and was not systematically related to treatment level. Control mortality after 48 h was 10 %, and within guideline limits. Control mortality was exceeded after 48 h only at an addition rate of 5600 mg/l of BW mud, and an approximate 48 h LC_{50} of 5400 mg/l was estimated using graphical interpolation (log-probability plot).

ACARTIA DEFINITIVE TESTS: EFFECTS AT 24 AND 48 H

Product hoursa	Treatment	24 hoursa No.	b	Mean %	48	b	Mean %	Expsd.
Base Oil	5600	0	0	0	0	0	0	20
	3200	0	0	0	0	0	0	21
	1800	0	0	0	0	2	10	20
	1000	0	0	0	0	0	0	20
MI Mud	5600	0	0	0	0	0	0	22
	3200	0	0	0	0	0	4.8	21
	1800	0	0	0	0	0	0	20
	1000	0	1	5	0	2	9.5	21
BW Mud	5600	0	0	0	4	8	60	20
	3200	1	1	10	1	0	5	20
	1800	0	0	0	0	0	0	20
	1000	0	0	0	1	1		10
20 Control			0	0	0	0	0	0

0 20 0 0 0 0 2 0 10 20

ANALYSIS AND INTERPRETATION

Skeletonema

None of the products tested (base oil, muds) caused a severe response in Skeletonema; addition rates of approximately 5000 mg/l or greater are clearly necessary to reduce growth rates by 50 %. It was observed that growth rates fluctuated considerably between successive 24 h periods, and that the greatest effects occurred during the 24-48 h interval. The reductions in effect over the final 24 h of the test may have been due either to a loss of test material from the vessels, or, more likely, due to the 'dilution' of effect as biomass increased and the 'load' of test substance per cell decreased (with corresponding increase in surface area for adsorption).

Acartia

None of the products tested (base oil, muds) caused a severe response in Acartia. A 48 h LC_{50} could be estimated only for BW mud, but this figure is approximate since a clear response was observed only at the highest concentration tested. As with the Skeletonema tests, the 50 % effects levels were clearly in the region of, or above, 5000 mg/l added substance.

Example 6

Blend Studies

Well fluid blend studies were made with paraffins, olefins and PAOs. The hydrocarbon blends set out in the tables below were formulated with olefins (dodecene-1 or tetradecene-1), paraffins (Paraffin-A, Paraffin-B or Paraffin-C, above) and PAOs (PAO-A or PAO-B, above). The blends were tested for viscometrics and flash point. The results below show that it is possible to achieve the desired viscometrics with the described blends according to the invention.

PAO-A BLEND STUDY

Blend A-	1	2	3	4	5	6	7	8	9
PAO-A	20	20	20	20	20	20	50	50	50
Dodecene-1	40	40	40				25	25	25
Tetradecene-1				40	40	40			
Paraff-A	40			40			25		
Paraff-B			40			40			25
Paraff-C			40			40			25
Visc. 100°C	0.71	0.80	0.88	0.81	0.92	1.01	0.99	1.06	1.13
40°C	1.72	1.95	2.18	1.99	2.26	2.52	2.59	2.79	2.99
Pour Pt. °C	-34	-28	-24	-26	-20	-15	-44	-40	-37
Flash Pt. °C	89	98	108	90	100	110	102	108	115

PAO-B BLEND STUDY

Blend B-	1	2	3	4	5	6	7	8	9	10	11	12
PAO-A	20	20	20	20	20	20	20	20	20	20	20	20
Dodecene-1	40	40	40							20	20	20
Tetradecene-1				40	40	40	20	20	20			
Paraff-A				40			60			60		
Paraff-B		40			40			60			60	
Paraff-C			40			40			60			60
Visc. 100°C	0.92	0.93	0.99	1.0	1.0	1.14	0.81	0.96	1.17	0.75	0.90	1.04
40°C	1.88	2.13	2.38	2.16	2.45	2.74	2.0	2.3	2.71	1.88	2.26	2.67
Pour Pt. °C	-26	-30	-8	-22	-12	-65	-28	-19	-3	-32	-23	-16
Flash Pt. °C	82	96	104	88	110	128	94	109	124	91	105	120

CLAIMS

1. A hydrocarbon blend of:

(i) a poly alpha-olefin (PAO) component having a viscosity of 1 to 6 cS and

(ii) a paraffinic hydrocarbon component of petroleum origin in the C_{10} - C_{18} range, and

(iii) an olefinic hydrocarbon component in the C_{10} - C_{18} range,

the proportions of the PAO component, the paraffinic hydrocarbon component and the olefinic hydrocarbon component being such that the blend has the following properties:

Viscosity at 100C	0.5 to 4 cS
Viscosity at 40C	1.0 to 30 cS
Pour point	not above +5C
Flash point	not less than 70C.

2. A blend according to claim 1 which has a viscosity at 100C from 0.7 to 2 cS and a viscosity at 40C from 2.0 to 20 cS.

3. A blend according to claim 1 or 2 which has a flash point of at least 100C.

4. A blend according to any preceding claim which has a pour point from -60 to 0C.

5. A blend according to any preceding claim in which the PAO component has a viscosity at 100C of 1 to 4 cS.

6. A blend according to any preceding claim in which the PAO component comprises an oligomer of a C_8-C_{18} 1-olefin.

7. A blend according to any preceding claim in which the amount of the PAO component is from 15 to 25 weight percent of the blend.

8. A blend according to any preceding claim in which the paraffinic hydrocarbon component comprises a fraction in the C_{12}-C_{16} range.

9. A blend according to any preceding claim in which the olefinic component comprises a 1-olefin in the C_{12}-C_{16} range.

10. A blend according to any preceding claim which includes the following components, in weight percent, based on the weight of the hydrocarbon blend:

dodecane	0 to 3
tetradecane	5 to 30
tetradecene	10 to 60
pentadecane	5 to 30
hexadecane	3 to 15
hexadecene	0 to 5
heptadecane	0 to 5
octadecane	0 to 5
eicosane	5 to 50
triacontane	2 to 40
tetracontane	0 to 5

11. A blend according to any preceding claim which includes the following components, in weight percent, based on the weight of the hydrocarbon blend:

dodecene	0.5 to 2
tetradecane	10 to 25
tetradecene	10 to 30
pentadecane	15 to 30
hexadecane	3 to 15
hexadecene	0.5 to 2
heptadecane	1 to 5
octadecene	0.5 to 2
eicosane	5 to 15
triacontane	5 to 10
tetracontane	0.5 to 2

12. A blend according to any preceding claim which includes the following components, in weight percent, based on the weight of the hydrocarbon blend:

dodecene	0.5 to 2
tetradecane	15 to 20
tetradecene	15 to 20
pentadecane	20 to 30
hexadecane	5 to 15
hexadecene	0.5 to 2

heptadecane	2 to 5
octadecene	0.5 to 2
eicosane	5 to 15
triacontane	5 to 10
tetracontane	0.5 to 2

13. A blend according to any preceding claim which includes the following components, in weight percent, based on the weight of the hydrocarbon blend:

decane	5 to 10
undecane	10 to 30
dodecane	20 to 30
tridecane	0 to 10
tetradecene	10 to 60
eicosane	5 to 50
triacontane	2 to 40
tetracontane	0 to 5

14. A blend according to any preceding claim which includes the following components, in weight percent, based on the weight of the hydrocarbon blend:

decane	5 to 10
undecane	20 to 30
dodecane	20 to 30
tridecane	2 to 5
tetradecene	10 to 30
eicosane	5 to 15
triacontane	5 to 10
tetracontane	0.5 to 2

15. A blend according to any preceding claim which includes the following components, in weight percent, based on the weight of the hydrocarbon blend:

dodecane	5 to 10
undecane	20 to 50
tetradecane	10 to 30
tetradecene	5 to 40
eicosane	5 to 50
triacontane	2 to 40
tetracontane	0 to 5

16. A blend according to any preceding claim which includes the following components, in weight percent, based on the weight of the hydrocarbon blend:

dodecane	5 to 10

	30 to 40
undecane	10 to 20
tetradecane	10 to 30
tetradecene	5 to 15
eicosane	5 to 10
triacontane	0.5 to 2
tetracontane	

17. A blend according to any preceding claim formulated as a well fluid.

18. A blend according to any preceeding claim formulated as a drilling mud.

19. Use of a well fluid or drilling mud of improved biodegradability and/or reduced marine toxicity according to claim 17 or 18 in a marine well-drilling operation in which drill cuttings containing the well fluid or drilling mud are discharged to the sea.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/07655

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C09K 7/00
US CL :507/103, 905
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 507/103, 905

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, Tulsa, Derwent drill and olefin#

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,096,883 (MERCER ET AL) 17 March 1992, see columns 1-12.	1-3
Y	US, A, 5,045,219 (TRAHAN ET AL) 03 September 1991, see columns 1-6.	1-3
Y	US, A, 4,876,017 (TRAHAN ET AL) 24 October 1989, see columns 1-10.	1-3
Y	US, A, 5,189,012 (PATEL ET AL) 23 February 1993, see columns 1-10.	1-3
Y	US, A, 4,525,285 (SON ET AL) 25 June 1985, see col. 5, lines 37-51.	1-3

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be part of particular relevance
- "E" earlier document published on or after the international filing date
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- "P" document published prior to the international filing date but later than the priority date claimed
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- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search 07 SEPTEMBER 1994	Date of mailing of the international search report SEP 27 1994
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